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(21)Application number : **59-210951** (71)Applicant : **MITSUBISHI ACETATE  
CO LTD**

(22)Date of filing : **08.10.1984** (72)Inventor : **SUZUKI SHIYOUJI  
NINOMIYA HIROFUMI  
YOSHII HIDEKI**

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## **(54) PARTIAL DEMETHOXYLATION METHOD OF PECTIN**

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### **SPECIFICATION**

#### **1. TITLE OF THE INVENTION**

Partial Demethoxylation Method of Pectin

#### **2. CLAIMS**

1. A partial demethoxylation method of a pectin characterized by treating the pectin by a sodium or potassium salt of carbonic acid or phosphoric acid.

2. A partial demethoxylation method of a pectin as set forth in claim 1, wherein the pectin is an aqueous solution of the pectin.

3. A partial demethoxylation method of a pectin as set forth in claim 1, wherein the pectin is a pectin-containing plant in a dry state, the sodium or potassium salt of carbonic acid or phosphoric acid is an aqueous solution, and the amount of the aqueous solution is not more than the weight of the plant in the dry state.

#### **3. DETAILED DESCRIPTION OF THE INVENTION**

##### **[Field of Utilization in Industry]**

The present invention relates to a partial demethoxylation method of a pectin. In more detail, the present invention relates to a method of partially demethoxylating an ester portion of partially methyl esterified D-galacturonic acid of a pectin to adjust the degree of methoxylation when extracting a pectin from a pectin-containing plant such as

citrus peel.

The properties of pectins differ according to the degree of methoxylation of the D-galacturonic acid in the pectin molecule. Pectins having a degree of methoxylation of 50% or more are classified as high methoxy (HM) pectins, while those having a degree of methoxylation of less than 50% are classified as low methoxy (LM) pectins. Further, in HM pectins, the gelation speed differs according to the degree of methoxylation thereof, so these pectins are classified as a rapid set, a medium set, and a slow set according to the degree of methoxylation thereof. In LM pectins, the properties such as the hardness of the gel and elasticity differ according to the degree of methoxylation, so the adjustment of the degree of methoxylation is important for producing a pectin.

[Prior Art]

For producing a pectin from a pectin-containing plant such as citrus peel, usually a dried pectin-containing plant is placed into an aqueous solution of an inorganic acid such as hydrochloric acid or sulfuric acid having a pH of 1.5 to 2.5 and stirred for 30 minutes to a few hours at 50°C to 100°C to extract the pectin component. Then, the insolubles of this extract are separated by centrifugal separation or pressing, the supernatant is filtered, then, according to need, condensed, then a water miscible solvent such as methanol, isopropyl alcohol, or acetone is added to cause precipitation or a salt of a metal such as aluminum, copper, or iron is added to cause the pectin to precipitate as a metal salt, and the result is dehydrated and recovered. In the case of the metallic salt method, it is necessary to wash the precipitate by an acidic alcohol or the like and eliminate the metal component to make it soluble. In any case, the precipitate of the pectin is dried and crushed to form a pectin powder.

If no adjustment of the degree of methoxylation is carried out in this process, though according to some extraction conditions, only pectins having a relatively high degree of methoxylation of for example 70 to 75% can be obtained, and only so-called rapid set type HM pectins can be obtained.

As the method of adjustment of the degree of methoxylation, there are known:

[1] a method of simultaneously performing the extraction and the adjustment of the degree of methoxylation by setting severe extraction conditions, for example, performing the extraction by acid over a long time or extracting the pectin by an aqueous solution containing a high concentration of acid;

[2] a method of treating the dehydrated and recovered pectin by an alcohol containing an acid; and

[3] a method of dipping a pectin-containing plant in an acidic solution.

[Problems to be Solved by the Invention]

However, the method of adjusting the degree of methoxylation at the time of extraction calls for treatment at high temperature such as 50 to 100°C for the purpose of advantageously performing the extraction, therefore also cleavage of glycoside bonds advances together with the demethoxylation, a drop in the molecular weight of the pectin, that is, a drop in the quality cannot be avoided, and, in certain cases, also the product yield is lowered.

The method of treating dehydrated and recovered pectin by an alcohol containing an acid calls for treatment at a relatively low temperature, therefore the drop in the quality of the pectin was small, but has the problems that the pectin has to be treated by an alcohol containing a high concentration of acid in an equal or greater amount to that of the pectin to be treated, so the cost of the used acid became high, it is necessary to neutralize the residual acid after the treatment, therefore alkali is required, and further a large amount of salt generated at the neutralization remains in the product, so washing has to be repeatedly carried out for removing this salt.

The method of dipping a dried pectin-containing plant in an acidic solution calls for dipping the plant in a 1 to 2N acidic aqueous solution of an amount a few times the amount of the plant and demethoxylating the result in a slurry state, but a considerably large amount of acid is used with respect to the amount of the plant to be treated. Therefore, according to some types of acid, there are the problem of corrosion of the equipment material in the production process and the problem that the amount of the salt generated due to the neutralization after the production is large and accordingly also the residual amount in the product becomes large.

Further, as a problem common to these methods, the demethoxylation by acid has an extremely slow reaction speed, therefore it is necessary to perform the treatment over a long time, and if the reaction temperature is made high as a countermeasure for this, a secondary reaction such as cleavage of the glycoside bonds occurs, which becomes a cause of a drop in the quality of the product.

#### [Means for Solving the Problems]

The gist of the present invention resides in a partial demethoxylation method of a pectin characterized by treating a pectin by a sodium or potassium salt of carbonic acid or phosphoric acid.

In the conventional treatment by an alkali, the reaction is fast, but it is difficult to control the reaction, and a drop in the quality of the product is induced, so it has been regarded as unsuitable. However, the inventors found that, if a suitable alkali was selected, the treat could be performed with a fast reaction speed without such a defect and thereby completed the present invention.

The alkali used in the present invention is a sodium or potassium salt of carbonic acid or phosphoric acid. Specifically, there can be mentioned sodium carbonate, sodium bicarbonate, potassium carbonate, potassium bicarbonate, disodium phosphate, dipotassium phosphate, trisodium phosphate, and tripotassium phosphate. They can be naturally also used in mixtures. A strong alkali such as sodium hydroxide and potassium hydroxide gives an extremely fast demethoxylation reaction, so it is difficult to control the reaction.

The amount of the alkali to be used is determined also according to the type of the used alkali, but the alkali may be added in a amount that keeps the pH of the system to about 9 to 10. Along with the advance of the demethoxylation, the pH of the system is lowered, therefore a weak alkali may be appropriately added or used together with the sodium carbonate or the sodium bicarbonate and so on.

The treatment of a pectin by these weak alkalis can be carried out in various steps in the production of a pectin. Namely, a pectin-containing plant can be treated too, or either of the extract obtained by extracting a pectin from a pectin-containing plant or a precipitate obtained by precipitating a pectin from this solution can be treated as well.

In the case of treating a pectin-containing plant, preferably a weak alkali aqueous solution of a weight about 3 times or more the weight of the plant is added to obtain a sufficiently homogeneous slurry state for the reaction.

When treating an extract or a solution obtained by removing the insolubles from this, a weak alcohol aqueous solution may be added to these solutions and mixed to cause the reaction. The ratio of the added solutions is not particularly limited. They may be added in amounts that can adjust the pH to within the above range.

In the case of treating a pectin precipitate, use is made of a mixed solution of a water miscible organic solvent and a weak alkali aqueous solution so as not to dissolve the precipitate. In order not to substantially dissolve the precipitate, the liquid ratio between the water and the water miscible organic solvent is set to 1/1 or less. As this water miscible organic solvent, methanol, ethanol, isopropyl alcohol, acetone, etc. can be exemplified. Preferably, use is made of a mixed solution of an equal weight with respect to the precipitate or a few times the amount of the precipitate. The mixing is carried out so that a sufficient homogeneous mixed solution is obtained. If the amount is less than an equal amount with respect to the precipitate, it tends to become hard to uniformly cause the reaction. When the amount is too large, it becomes economically disadvantageous due to the recovery of the solvent and according to the amount of the used alkali etc.

No matter at which of these steps the alkali treatment is carried out at, preferably

the temperature of the reaction system is held at 30°C or less. When it exceeds 30°C,  $\beta$ -elimination of the glycoside bonds proceeds and there may be an effect upon the quality of the pectin, so this is not preferred.

#### [Examples]

The present invention will be explained in further detail below by using examples.

Note that, in the examples, the jelly grade was evaluated by the IFT method (*Food Technology*, Vol. 13, 496-500 (1959)), and the degree of methoxylation was according to the corrosion titration method disclosed in the *Food Chemicals Codex*, 3rd edition.

#### Example 1

400 g of dried peel of squeezed lemons was placed in 4 liters of water in which 30 g of potassium carbonate was dissolved, then was stirred, mixed, and allowed to stand for 2 hours. The water temperature was 15°C. Next, 10 liters of water was added to this mixed solution, then this was stirred and was controlled in pH to 2.0 by using hydrochloric acid, was elevated in temperature, and was stirred and extracted at 90°C for 30 minutes. Next, the insolubles were centrifugally separated and removed, 0.5% of a diatomaceous earth filter aid was added to the obtained supernatant, then the result was filtered under pressure to obtain 7.8 kg of clear filtrate. To this filtrate, isopropyl alcohol was added so as to obtain a 60 vol% concentration. The thus precipitated precipitate of the pectin was separated, pressed, dried, and crushed, thereby to obtain 64 g of a pectin powder. The degree of methoxylation of the obtained pectin was 60.5%, and the jelly grade was 199.

#### Example 2

400 g of dried peel of squeezed lemons was placed in 3.5 liters of water in which 20 g of trisodium phosphate was dissolved, then was stirred, mixed, and allowed to stand at a water temperature of 15°C for 1.5 hours. Below, the extraction and purification were carried out in the same way as Example 1 to obtain a pectin powder. The degree of methoxylation of the obtained pectin was 63.6%, and the jelly grade was 193.

#### Example 3

400 g of dried peel of squeezed lemons was placed in 4 liters of water in which 23 g of sodium carbonate and 6 g of sodium bicarbonate were dissolved, then was stirred, mixed, and allowed to stand at a water temperature of 15°C for 3 hours. Below, the extraction and purification were carried out in the same way as Example 1 to obtain a pectin powder. The degree of methoxylation of the obtained pectin was 59.7%, and the

jelly grade was 203.

**Example 4**

Water was added to 300 g of dried peel of squeezed oranges to 10 liters, then the result was controlled in pH to 2.0 by using hydrochloric acid, was elevated in temperature, and was stirred and extracted at 90°C over 30 minutes. This extract was cooled to 25°C, then 500 ml of water in which 30 g of potassium carbonate was dissolved was added and mixed. The result was reacted for 2 hours, then neutralized by hydrochloric acid. Then, the insolubles were removed by centrifugal separation, and 0.5% of a diatomaceous earth filter aid was added to the obtained supernatant which was then filtered under pressure to obtain a clear filtrate. To this filtrate, isopropyl alcohol was added to a 60 vol% concentration, then the thus precipitated precipitate of pectin was separated, dried, and crushed, thereby to obtain a pectin powder. The degree of methoxylation of the obtained pectin was 62.5%, and the jelly grade was 193.

**Example 5**

300 g of dried peel of squeezed lemons was extracted in the same way as Example 4. The insolubles were removed from this extract to obtain 8.0 liters of a clear filtrate. This filtrate was cooled to 20°C, and then mixed with 500 ml of water in which 21 g of sodium carbonate and 6 g of sodium bicarbonate were dissolved, reacted for 3 hours, then neutralized by hydrochloric acid, and treated in the same way as Example 1, to thereby obtain a pectin powder. The degree of methoxylation of the obtained pectin was 57.6%, and the jelly grade was 196.

**Example 6**

Water was added to 300 g of dried peel of squeezed lemons to 10 liters, then the result was controlled in pH to 2.0 by using hydrochloric acid, was elevated in temperature, and was stirred and extracted at 90°C over 30 minutes. Next, the insolubles were removed by centrifugal separation, and 0.5% of a diatomaceous earth filter aid was added to the obtained supernatant, which was then filtered under pressure to obtain 8.3 kg of a clear filtrate. To this filtrate, isopropyl alcohol was added to 60 vol% concentration, then the thus precipitated precipitate of pectin was separated and pressed to obtain 225 g of a precipitate with a 25% solids concentration. To this precipitate, 400 ml of isopropyl alcohol having a 60 vol% concentration in which 3 g of potassium carbonate was dissolved was added. The result was stirred, mixed, and reacted for 1 hour. Below, the neutralization, filtration, pressing, drying, and crushing were carried out in the same way as Example 5 to obtain a pectin powder. The degree of methoxylation of the obtained pectin was 62.0 %, and the jelly grade was 193.

**Comparative Example 1**

The extraction, purification, drying, and crushing were carried out in the same way as Example 1 to obtain pectin except for not pretreating 400 g of dried peels of squeezed lemons and oranges by weak alkali. The degree of methoxylation of the pectin from the dried peel of squeezed lemons was 73.3% and the jelly grade was 208, while the degree of methoxylation of the pectin from the oranges was 67.8%, and the jelly grade was 185.

[Effect of the Invention]

As apparent from the above examples, the invention of the present application adjusting the degree of methoxylation of a pectin by using a sodium or potassium salt of carbonic acid or phosphoric acid has the excellent effects that the degree of methoxylation can be adjusted in a short time and, in addition, the drop in the quality of the pectin due to the alkali which had been conventionally reported is not induced.